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# (54) METHOD FOR MANUFACTURING INKJET RECORDING SHEET

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing an inkjet recording sheet having high resistance to crazing and high glossiness with good coating properties.

SOLUTION: In the method (1), a coating layer of a boric acid-containing solution is provided on an inside ink receiving layer on a substrate and a coating liquid comprising a polymer performing crosslinking reaction 231 with boric acid is applied thereon and drying is performed while the polymer is crosslinked to form an outside ink receiving layer. In the method (2), the coating layer of the boric acid-containing solution is provided on an outside ink receiving layer formed on a transfer base material and the coating liquid comprising the polymer performing the crosslinking reaction with boric acid is applied thereon and drying is performed while the polymer is crosslinked to form the inside ink receiving layer and after the substrate is stuck thereon, the transfer base material is released.



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#### **CLAIMS**

# [Claim(s)]

[Claim 1] On a base material, the inside ink absorbing layer containing a resin ingredient and a pigment of at least one layer is formed. It includes forming the outside ink absorbing layer containing a resin ingredient and a pigment on said inside ink absorbing layer. The manufacture approach of the ink jet record sheet characterized by making said resin ingredient of the outside ink absorbing layer which applies a boric acid content solution and is formed on it on said inside ink absorbing layer contain the polymer in which the crosslinking reaction by boric acid is possible on the occasion of formation of said outside ink absorbing layer.

[Claim 2] On an imprint base material, the outside ink absorbing layer containing a resin ingredient and a pigment is formed. On said outside ink absorbing layer, the inside ink absorbing layer containing a resin ingredient and a pigment of at least one layer is formed. A base material is stuck on the front face of said inside ink absorbing layer on said imprint base material. Formation of said inside ink absorbing layer is faced said imprint base material including exfoliating from this attachment object. The manufacture approach of the ink jet record sheet characterized by making said resin ingredient in the inside ink absorbing layer which applies a boric acid content solution and is formed on it on said outside ink absorbing layer contain the polymer in which crosslinking reaction is possible with boric acid.

[Claim 3] The manufacture approach of an ink jet record sheet given in claim 1 or two publications which include further forming the inside ink absorbing layer which contains the polymer in which crosslinking reaction is possible in a resin ingredient with boric acid on the inside ink absorbing layer in which said inside ink absorbing layer was formed in more than two-layer, and was formed previously after applying a boric acid content solution.

[Claim 4] The polymer in which crosslinking reaction is possible with said boric acid Polyvinyl alcohol, Cation denaturation polyvinyl alcohol, silyl denaturation polyvinyl alcohol, A polyvinyl acetal, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, Casein soybean protein, synthetic protein, starch, polypropylene oxide, A polyethylene glycol, polyvinyl ether, polyvinyl acrylamide, The manufacture approach of an ink jet record sheet given in any 1 term of claims 1–3 chosen from a polyvinyl pyrrolidone, a styrene-butadiene copolymer, a methylmetaacrylate, and a styrene-vinyl acetate copolymer.

[Claim 5] The manufacture approach of an ink jet record sheet given in any 1 term of claims 1-4 in which the pigment contained in said outside ink absorbing layer and an inside ink absorbing layer contains at least one sort chosen from the group which consists of a silica, aluminosilicate, an alumina, and hydrated alumina independently of others, respectively.

[Claim 6] The manufacture approach of an ink jet record sheet given in any 1 term of claims 1-5 whose content of the resin ingredient contained in said outside ink absorbing layer and an inside ink absorbing layer is the 3 - 100 mass section to the pigment 100 mass section independently of others, respectively.

[Claim 7] The content of said boric acid crosslinking bond possible polymer to the sum total mass of said resin ingredient of the outside ink absorbing layer containing the polymer by said boric acid in which crosslinking reaction is possible, and an inside ink absorbing layer is the manufacture approach of an ink jet record sheet given in any 1 term of claims 1-6 which is 50 to

100 mass % independently of others, respectively.

[Claim 8] the boric acid content of said ink jet record sheet — 0.025 – 2.5 g/m2 it is — the manufacture approach of an ink jet record sheet given in any 1 term of claims 1–7. [Claim 9] The manufacture approach of an ink jet record sheet given in any 1 term of claims 1–8 whose 75-degree surface glossiness (JIS-Z -8741) of said ink jet record sheet is 30% or more.

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#### **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[Field of the Invention] Ink absorptivity and lightfastness of this invention are good, and, moreover, defects, such as a crack, are related with the approach of manufacturing an glossy high ink jet record sheet with sufficient spreading nature few. [0002]

[Description of the Prior Art] Water color ink is blown off from a detailed nozzle toward a record sheet, and the ink jet recording method which makes an image form on record dignity is widely used by the terminal printer, facsimile, the plotter, or document printing for the reasons that there is little noise at the time of record, that formation of a full color image is easy, that highspeed record is possible, nil why record cost is cheaper than other airline printers, etc. [0003] On the other hand, the advancement of a property came to be requested also from the record sheet by the appearance of a digital camera at the rapid spread of printers, a high definition and improvement in the speed, and a pan. That is, implementation of the record sheet which combines the image quality which is excellent in absorptivity, record concentration, a water resisting property, and lightfastness, and is equal to the photograph of a silver salt method, and shelf life is called for strongly. Furthermore, in order to bring a record product close with a photograph product, the glossy improvement in a high record sheet is also demanded. [0004] The method of graduating the front face of an ink absorbing layer on a record object by carrying out heating pressurization by Hazama of one pair of rolls is learned using equipments. such as a supercalender, as an approach of generally giving glossiness to a record sheet. However, in order that the ink absorptivity openings from which it is distributed in an ink absorbing layer may decrease in number, the phenomenon in which a blot occurs in an ink image is in the top where such an approach of the glossiness acquired is inadequate as a result. In order to realize the image of the photograph tone which does not especially have a granular feeling at the latest ink jet printer, the record sheet is asked for higher ink absorptivity when the printer of photograph ink loading which carries out the overprint of the low concentration ink is becoming in use.

[0005] In order to acquire high ink absorptivity, it is necessary to make coverage of an ink absorbing layer abundant. For example, as indicated to JP,2000–301828,A, when usually forming an ink absorbing layer with high coverage (30 micrometers or more as desiccation thickness), the humid film of coating liquid needs to be applied by 100-micrometer high thickness. When drainage system coating liquid is applied on a base material by such high humid thickness, the problem that a crack tends to occur is in an ink absorbing layer at the time of the desiccation. As this reason, since the ink absorption layer formed is the hard film, if this is dried quickly, a crack will occur or it will be considered for producing the liquid kink (the coating on a base material moving by the wind) by the wind.

[0006] Therefore, in JP,2000-301828,A, it has proposed applying the coating liquid which forms the 1st porous layer on a non-absorptivity base material, drying, applying the coating liquid which forms the 2nd porous layer with desiccation thickness thinner than the 1st porous layer behind, and making it dry. However, forming many ink absorbing layers thinly, respectively, and carrying

out the laminating of these may have high process cost, and it may produce a problem economically. However, a means effective [ there are as much as possible few cracks of a coating layer, and ] in order to obtain thick thickness is not indicated at all by the abovementioned official report.

[0007] In order to form the ink absorbing layer which has high ink absorptivity, it is required to decrease the content of the binder in an ink absorbing layer generally. However, if it does so, the problem that the paint film reinforcement of an ink absorbing layer falls will be produced. In order to solve this problem, in JP,4–223190,A, they are borax or boric acid 0.1 g/m2 Using the base paper to which the above amount of coating was applied is proposed. Moreover, preparing borax or a boric acid processing layer in the glossy surface of a piece glazed paper is proposed by JP,5–104848,A. Furthermore, the art which makes the gelling agent of a binder cloth at the time of \*\* is proposed by JP,7–238467,A. Furthermore, using the base material in which surface treatment was carried out by the paper finishing agent which consists of one or more sorts chosen from the group which consists of boric acid and borate is proposed by JP,11–115308,A. They are boric acid or a boron compound on the field which has furthermore countered the color–material acceptance layer of this base material between a base material and a color–material acceptance layer at JP,2001–246832,A 0.1 g/m2 Carrying out coating by the above coverage is proposed.

[0008] However, when using non-absorptivity base materials, such as resin covering paper, it is impossible to infiltrate a boron compound into this base material. Moreover, though are easy to thicken this coating liquid, and it is hard coming to carry out coating for this reason and coating can be carried out if a boron compound is added in the coating liquid for ink absorbing layers in order to make an ink absorbing layer contain a boron compound When the coating liquid for additional ink absorbing layers is further applied on this ink absorbing layer, it is difficult to elute boric acid with the amount which can construct a bridge in the binder in it into the ink jet acceptance layer of this addition, and it has the problem that that effectiveness is low.

[0009] In the sheet for record with which it comes to prepare a color-material acceptance layer at JP,11–115308,A on a base material This color-material acceptance layer applies the coating liquid containing a non-subtlety particle and water soluble resin on a base material. This spreading and coincidence, or before this applied layer comes to show the falling rate of drying, giving the solution containing the cross linking agent over which said water soluble resin can be made to construct a bridge to said coating liquid layer, and making it harden said coating liquid layer is proposed.

[0010] However, since the bridge formation rate was slow, it was easy to produce the liquid kink depended a style, and this invention persons' examination showed that control of a crack was inadequate. Therefore, there is no thickening of the coating for ink absorbing layers, and, moreover, the present condition is that bridge formation of an ink absorbing layer compatible [ crack prevention of a coating layer and liquid kink prevention ] is difficult.

[0011] Furthermore, the coloring matter image fading inhibitor is proposed by JP,57-74192,A. Moreover, making an ink absorbing layer contain a hindered amine system compound is proposed by JP,61-146591,A. Furthermore, making an ink absorbing layer contain an ultraviolet ray absorbent and an antifungal agent is proposed by JP,62-261476,A. However, although indicated by these reference about amelioration of the lightfastness of an ink image, a crack prevention means is not indicated at all.

[0012]

[Problem(s) to be Solved by the Invention] This invention is excellent in spreading nature, ink absorptivity and its lightfastness are good, and, moreover, defects, such as a crack, tend to offer the manufacture approach of an glossy high ink jet record sheet few.
[0013]

[Means for Solving the Problem] The manufacture approach (1) of the ink jet record sheet of this invention On a base material, the inside ink absorbing layer containing a resin ingredient and a pigment of at least one layer is formed. It includes forming the outside ink absorbing layer containing a resin ingredient and a pigment on said inside ink absorbing layer. It is characterized by making said resin ingredient of the outside ink absorbing layer which applies a boric acid

content solution and is formed on it on said inside ink absorbing layer contain the polymer in which the crosslinking reaction by boric acid is possible on the occasion of formation of said outside ink absorbing layer. The manufacture approach (2) of the ink jet record sheet of this invention On an imprint base material, the outside ink absorbing layer containing a resin ingredient and a pigment is formed. On said outside ink absorbing layer, the inside ink absorbing layer containing a resin ingredient and a pigment of at least one layer is formed. A base material is stuck on the front face of said inside ink absorbing layer on said imprint base material. Formation of said inside ink absorbing layer is faced said imprint base material including exfoliating from this attachment object. It is characterized by making said resin ingredient in the inside ink absorbing layer which applies a boric acid content solution and is formed on it on said outside ink absorbing layer contain the polymer in which crosslinking reaction is possible with boric acid. In the manufacture approach (1) of the ink jet record sheet of this invention, and (2), you may include further forming the inside ink absorbing layer which contains the polymer in which crosslinking reaction is possible in a resin ingredient with boric acid on the inside ink absorbing layer in which said inside ink absorbing layer was formed in more than two-layer, and was formed previously, after applying a boric acid content solution. In the manufacture approach (1) of the ink jet record sheet of this invention, and (2) The polymer in which crosslinking reaction is possible with said boric acid Polyvinyl alcohol, Cation denaturation polyvinyl alcohol, silyl denaturation polyvinyl alcohol, A polyvinyl acetal, methyl cellulose, ethyl cellulose. hydroxyethyl cellulose, Casein soybean protein, synthetic protein, starch, polypropylene oxide. It is desirable to be chosen out of a polyethylene glycol, polyvinyl ether, polyvinyl acrylamide, a polyvinyl pyrrolidone, a styrene-butadiene copolymer, a methylmetaacrylate, and a styrene-vinyl acetate copolymer. In the manufacture approach (1) of the ink jet record sheet of this invention, and (2), it is desirable that at least one sort as which the pigment contained in said outside ink absorbing layer and an inside ink absorbing layer was chosen from the group which consists of a silica, aluminosilicate, an alumina, and hydrated alumina respectively independently of others is included. In the manufacture approach (1) of the ink jet record sheet of this invention, and (2), it is desirable that the content of the resin ingredient contained in said outside ink absorbing layer and an inside ink absorbing layer is the 3 - 100 mass section to the pigment 100 mass section independently of others, respectively. As for the content of said boric acid crosslinking bond possible polymer to the sum total mass of said resin ingredient of the outside ink absorbing layer containing the polymer by said boric acid in which crosslinking reaction is possible, and an inside ink absorbing layer, in the manufacture approach (1) of the ink jet record sheet of this invention. and (2), it is desirable respectively that it is 50 - 100 mass % independently of others, the manufacture approach (1) of the ink jet record sheet of this invention, and (2) --- setting -- the boric acid content of said ink jet record sheet -- 0.025-2.5g/m2 it is -- things are desirable. In the manufacture approach (1) of the ink jet record sheet of this invention, and (2), it is desirable that 75-degree surface glossiness (JIS-Z -8741) of said ink jet record sheet is 30% or more.

[Embodiment of the Invention] (The coating approach) In this invention approach (1), the inside ink absorbing layer containing a resin ingredient and a pigment of at least one layer is formed on a base material, and the outside ink absorbing layer containing a resin ingredient and a pigment is formed on said inside ink absorbing layer. On the occasion of formation of this outside ink absorbing layer, into the resin ingredient of the coating liquid for outside ink absorbing layers, the polymer which can carry out crosslinking reaction with boric acid is included, a boric acid content solution is applied on said inside ink absorbing layer, the coating liquid containing the polymer which carries out crosslinking reaction with said boric acid on it is applied, it dries and an outside ink absorbing layer is formed.

[0015] In this invention approach (2), the outside ink absorbing layer containing a resin ingredient and a pigment is formed on the shaping front face of an imprint base material, the inside ink absorbing layer containing a resin ingredient and a pigment of at least one layer is formed on it, a base material is stuck on this inside ink absorbing layer, said imprint base material is exfoliated from this attachment object, and an ink jet record sheet is obtained. The polymer which can construct [ be / it / under / resin ingredient / of the coating liquid for forming the inside ink

absorbing layer which touches an outside ink absorbing layer directly / reaction ] a bridge with boric acid is made to contain on the occasion of formation of said inside ink absorbing layer, a boric acid content solution is applied on the outside ink absorbing layer on an imprint base material, the coating liquid for inside ink absorbing layers containing the polymer which can carry out crosslinking reaction with said boric acid on it is applied, and it dries.

[0016] If a boric acid content solution spreading layer and the coating liquid layer for an outside or inside ink absorbing layers containing the polymer which can construct a bridge with boric acid contact, since coating liquid will gel immediately and it will become a passive state, it is hard to generate the liquid kink by the wind, and it becomes possible to enlarge airflow at the time of desiccation for this reason, and to raise drying efficiency. Moreover, the outside ink absorbing layer after desiccation also shows high resistance to a crack.

[0017] After applying a boric acid content solution and giving a desiccation process, the coating liquid for an outside or inside ink absorbing layers containing the polymer which can construct a bridge with boric acid may be applied. However, it is desirable to apply the coating liquid for ink absorbing layers from the point of the gelation effectiveness of the coating liquid for ink absorbing layers, while a boric acid content solution spreading layer is in a damp or wet condition. Desirable moisture regain in case a boric acid content solution spreading layer contacts the coating liquid for ink absorbing layers is 30% or more, and is 50% or more more preferably. In addition, the inside ink absorbing layer previously formed when at least two layers of inside ink absorbing layers were prepared (namely, it sets to the manufacture approach (1) of this invention) In the manufacture approach (2) of an inside ink absorbing layer and this invention formed on the base material The coating liquid for inside ink absorbing layers for the inside ink absorbing layer formed on the outside ink absorbing layer on an imprint base material to form it is applied. It dries, and after being formed, a boric acid content solution may be applied on this inside ink absorbing layer formed previously, the coating liquid for inside ink absorbing layers which contains the polymer which can construct a bridge in response to a it top with boric acid may be applied, and the inside ink absorbing layer over which the bridge was constructed by drying may be formed.

[0018] In this case, after applying a boric acid content solution on the inside ink absorbing layer formed previously like the above and drying this, the coating liquid for inside ink absorbing layers containing the polymer which can construct a bridge with boric acid on it may be applied. However, while a boric acid content solution spreading layer is in a damp or wet condition from the point of the gelation effectiveness of coating liquid, it is desirable to apply the coating liquid for inside ink absorbing layers containing the polymer in which boric acid bridge formation is possible. The moisture regain with the desirable boric acid content solution spreading layer at this time is 30% or more, and is 50% or more more preferably.

[0019] In drawing 1, the ink jet record sheet 6 obtained by this invention approach (1) and (2) is constituted by the base material 1, the inside ink absorbing layer 2 formed on it, and the outside ink absorbing layer 3 formed on it. When an ink jet record sheet is formed by this invention approach (1) In the condition that apply a boric acid content solution spreading layer on it, and it has 50% or more of moisture regain preferably although it is not illustrated after forming the inside ink absorbing layer 2 on a base material 1 (desiccation) Although a boric acid content solution spreading layer will disappear if the outside ink absorbing layer 3 is formed on it and it dries Crosslinking reaction of the polymer which can carry out crosslinking reaction to the boric acid in an outside ink absorbing layer is carried out to boric acid, and outside ink absorbing layer coating liquid gels it, it can perform coexistence of crack prevention of an outside ink absorbing layer, and liquid kink prevention, and, moreover, binds the outside ink absorbing layer 3 to the inside ink absorbing layer 2 firmly. It is drawing 2 when an ink jet recording layer is manufactured by this invention approach (2) in drawing 2 . - The outside ink absorbing layer 3 is formed on the imprint base material 4, and the boric acid content solution spreading layer 5 is formed on it as shown in (A). Next, drawing 2 - In the condition that said boric acid solution spreading layer 5 has 50% or more of moisture regain preferably as shown in (B) Although the inside ink absorbing layer 2 is formed on the boric acid content solution spreading layer 5, crosslinking reaction of the polymer which can carry out crosslinking reaction to the boric acid in the inside ink

absorbing layer 2 will be carried out to boric acid and the boric acid content solution spreading layer 5 will disappear after the desiccation if it dries, the inside ink absorbing layer 2 is firmly bound to the outside ink absorbing layer 3. Next, drawing 2 - A base material 1 is bound on the inside ink absorbing layer 2 as shown in (C). Desiccation solidification of the inside ink absorbing layer may be carried out carrying out the laminating of the base material 2, and binding it at this time, before an inside ink absorbing layer dries, and after carrying out desiccation solidification of it, adhesives or water may be applied to a spreading layer, and it may be stuck to a base material 1 by pressure. Next, drawing 2 - The imprint base material 4 is exfoliated from the record sheet 6 which consists of base material 1 / inside ink absorbing layer 2 / an outside ink absorbing layer 3 as shown in (D).

[0020] (Base material) In this invention approach, \*\*\*\* use of the sheets, such as papers, such as films, such as cellophane, polyethylene, polypropylene, plasticized polyvinyl chloride, rigid polyvinyl chloride, and polyester, paper of fine quality, art paper, a metallic paper, kraft paper, resin covering paper, an impregnated paper, and vacuum evaporationo paper, metal foil, and a synthetic paper, is carried out as a base material. Moreover, coated paper, such as coat paper and cast paper, and the thing which prepared the well-known ink absorbing layer beforehand may be used, for example.

[0021] In the record sheet of this invention, if the covering paper or the synthetic papers by resin, such as polyethylene and polypropylene, are used as a base material in order to prevent the cock ring and to raise surface smooth nature and surface glossiness, since it will become possible to record the ink image which has the image quality which is equal to the photograph of a silver salt method, these are used especially preferably.

[0022] When resin covering paper is used as a base material, it is effective to have the purpose which raises the adhesion of a base material and an inside ink absorbing layer, and to perform adhesion processing or adhesion processing to an inside ink absorbing layer side beforehand. Moreover, at the base material rear face, you may process as occasion demands for conveyance nature, electrification prevention, blocking prevention, etc. although there is especially no limitation in the smoothness of a base material — high gloss and quantity — in order to obtain the ink jet record sheet which has a smooth front face, it is desirable to use the base material which has the smoothness more than 300 second (Oken type, J.TAPPI NO5). Moreover, although there is especially no limitation also in the opacity of a base material, in order to obtain film—photo—like aesthetic property, it is desirable that the opacity (JIS P8138) of a base material is 85% or more.

[0023] (Imprint base material) \*\*\*\* use of the drum on which the product made from sheets, such as papers, such as plastic film, such as the cellophane which has for example, the Takahira slippage, polyethylene, polypropylene, plasticized polyvinyl chloride, rigid polyvinyl chloride, and polyester, resin covering paper, glassine, an impregnated paper, vacuum evaporationo paper, and water-soluble paper, metal foil, and a synthetic paper, inorganic glass, a metal, or plastics carries out the Takahira slippage shaping \*\*\*\*\*\* of the imprint base material used for the manufacture approach (2) of this invention, and the plates be carried out. It is desirable to use especially the metal drum which has plastic film and the Takahira slippage, in view of the engine performance of a production process and the shaping side of a spreading layer. In order that the shaping side of an imprint base material may give the gloss excellent in the record sheet, the smoother one is desirable, as for surface roughness Ra (JIS-B -0601) of a shaping side, it is desirable that it is 0.5 micrometers or less, and it is 0.05 micrometers or less more preferably. However, surface roughness can be controlled suitably and front faces, such as a semi gross tone, can also be given to a record sheet.

[0024] (An outside ink absorbing layer and inside ink absorbing layer) The outside ink absorbing layer and inside ink absorbing layer which have a resin ingredient (binder) and a pigment are explained.

[0025] (Pigment) The pigments used for an ink absorbing layer are amorphous silica (the cation denaturation silica by an alumina etc. is included), a kaolin, clay, baking clay, a zinc oxide, the tin oxide, magnesium sulfate, an aluminum hydroxide, an alumina and hydrated alumina, a calcium carbonate, a satin white, aluminum silicate, a smectite, a zeolite, a magnesium silicate, a

magnesium carbonate, magnesium oxide, diatomaceous earth, a styrene system plastics pigment, a urea-resin system plastics pigment, a benzoguanamine system plastics pigment, etc. It is desirable to use the silica which the balance of glossiness and ink absorptivity tends to take, aluminosilicate, an alumina, and hydrated alumina in this invention.

[0026] As for especially the pigment contained from an glossy point in an outside ink absorbing layer (that is, place which ink reaches first), it is desirable that the particle diameter is a pigment 1 micrometer or less. It is more desirable that the first [ an average of ] particle diameter is 3–40nm, and the second [ an average of ] particle diameter is furthermore a pigment 500nm or less. If the second [ an average of ] particle diameter exceeds 1 micrometer, the smooth nature of an outside ink absorbing layer will fall, therefore the glossiness will also fall. A precise outside ink absorbing layer is formed as the first [ an average of ] particle diameter is less than 3nm, and for this reason, ink absorptivity falls.

[0027] It is obtained by there being especially no limit in the distributed approach of a pigment, for example, giving the strong force to the synthetic amorphous silica (several micrometers) of general marketing by the mechanical means. As a mechanical means, the mechanical technique of a supersonic wave, a high-speed tumbling mill, a roller mill, a container drive medium mill, a solvent agitation mill, a jet mill, a Sand grinder, etc. is mentioned. Although especially a dispersion-medium object is not limited, water is used, for example.

[0028] As long as it can construct a bridge over the polymer which it is used in this invention approach (1) and (2), and can carry out crosslinking reaction with boric acid with boric acid, there is no limit according to rank, for example, polyvinyl alcohol, cation denaturation polyvinyl alcohol, silyl denaturation polyvinyl alcohol, a polyvinyl acetal, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, casein, soybean protein, synthetic protein, starch, polypropylene oxide, a polyethylene glycol, polyvinyl ether, polyvinyl acrylamide, a polyvinyl pyrrolidone, etc. are mentioned. In addition, various adhesives (for example, vinyl system copolymer latexes, such as a conjugated diene system polymer latex [ of a styrene-butadiene copolymer and a methyl methacrylate-butadiene copolymer ], acrylic polymer latex, and styrene-vinyl acetate copolymer etc.) generally used in the coated paper field, such as water-dispersion resin, may be used within limits by which the purpose of this invention is attained.

[0029] In this invention approach (1) and (2), the various water soluble resin which includes polyvinyl alcohol for ink absorptivity, a paint film water resisting property, crack prevention, etc. is preferably used as a polymer which can carry out crosslinking reaction to boric acid. Polyvinyl alcohol is used more preferably, it is desirable that it is 3000 or more, however, as for the polymerization degree, it is desirable that it is 5000 or less. The water resisting property of the ink absorbing layer where polymerization degree is acquired less than by 3000 is inadequate. Moreover, that to which it exceeds 5000 is difficult to receive practically.

[0030] (Solid content mass ratio of a pigment and a polymer) In this invention approach (1) and (2), although there is especially no limit in the solid content mass ratio of the pigment and resin ingredient which are used for an outside ink absorbing layer and an inside ink absorbing layer, it is desirable that a resin ingredient is the 3 – 100 mass section to the pigment 100 mass section, and it is 5 – 30 mass section more preferably. If the content ratio of a resin ingredient is too high, the pore formed between pigment particles may become small, and ink absorptivity may fall. There is a possibility that it may be easy to be generated in the ink absorbing layer obtained as too little [ the content ratio of a resin ingredient ] on the other hand, and it may become impossible to use a crack for it.

[0031] (Boric acid content solution) Since it has the property which promotes gelation of the coating liquid layer containing the polymer in which the crosslinking reaction in a resin ingredient is possible in this invention approach (1) and (2) even when boric acid is little, the spreading nature of the ink absorbing layer containing the above-mentioned polymer improves, and the ink absorptivity of the ink absorbing layer moreover obtained improves, and lightfastness also improves, the boric acid content of an ink jet record sheet — 0.025 – 2.5 g/m2 it is — things are desirable. It or 0.025 g/m2 In the following, the effectiveness of the request to the record sheet obtained is hard to be acquired, and it is 2.5 g/m2. If it exceeds, the effectiveness acquired by containing boric acid will be saturated upwards, and problems — a spreading layer becomes easy

to crack with water or humidity -- will be produced.

[0032] As for the boric acid concentration of a boric acid content solution, it is desirable that it is 0.01 to 4 mass %. If it becomes difficult for it to acquire desired effectiveness in the record sheet obtained at less than 0.01% and it exceeds 4%, since the boric acid solubility in a solution will be saturated, a manufacturing cost will increase unnecessarily.

[0033] (Cationic compound) A cationic compound may be added all over the outside of this invention, and/or the inside ink absorbing layer of at least one layer. Thereby, it can raise ink fixable. As a cationic compound added, polyalkylene polyamine, such as a polyethylene amine and polypropylene polyamine, or the derivative of those, the acrylic resin that has the 3rd class amino group and the 4th class ammonium, a JIAKURIRU amine, etc. are mentioned, for example. In addition, as an addition of cation resin, to the pigment 100 mass section, it is desirable that it is 1 – 30 mass section, and it is more preferably adjusted within the limits of 5 – 20 mass section. Moreover, all over each ink absorbing layer, various assistants, such as the dispersant used in common coated paper manufacture, a thickener, a defoaming agent, a coloring agent, an antistatic agent, and antiseptics, may be added mutually—independent, respectively.

[0034] Although there is especially no limitation in the coverage of the sum total of an outside ink absorbing layer and an inside ink absorbing layer in this invention approach (1) and (2), it is 5 – 60 g/m². Adjusting to extent is desirable. Coverage is 5 g/m². When few, the ink absorptivity and image quality of an ink absorbing layer which are acquired may become inadequate, and coverage is 60 g/m². If many, it will become easy to produce a crack in the ink absorbing layer obtained, in order for the image quality which is equal to the photograph of a silver salt method to obtain — the sum total coverage of an ink absorbing layer — 20 – 45 g/m² it is — things are desirable.

[0035] The coating liquid layer for ink absorbing layers first formed on a base material or an imprint base material can apply and form the coating liquid for ink absorbing layers using various coating equipments, such as for example, a blade coating machine, an air knife coating machine, a roll coater, a bar coating machine, a gravure coating machine, a rod FUREDO coating machine, a lip coating machine, a die coating machine, and a curtain coating machine, and the ink absorbing layer which dried this and was solidified can be obtained.

[0036] In order to form the ink absorbing layer of a two-layer eye on a base material or an imprint base material On the ink absorbing layer of the 1st layer prepared previously, a blade coating machine, an air knife coating machine, A roll coater, a bar coating machine, a gravure coating machine, a rod FUREDO coating machine, After applying a boric acid content solution by the curtain coating machine, a die coating machine, etc., on it, one or more of the same various coating equipments of the as the 1st layer are used, it can apply and dry and the coating liquid for ink absorbing layers of a two-layer eye can be obtained.

[0037] What is necessary is to apply the coating liquid for ink absorbing layers containing the polymer which can construct a bridge with boric acid, and just to repeat the process to dry, after applying said boric acid content solution, also when, preparing the ink absorbing layer after the 3rd layer, of course.

[0038] Unless the effectiveness of a request of this invention is checked, the pigment except said, a surface active agent, adhesive resin, a gas—proof improver, an anti-oxidant, an ultraviolet ray absorbent, a mold inhibitor, a cationic compound, a fluorescent brightener, a color, etc. may be made to contain all over an outside and an inside ink absorbing layer.

[0039] In this invention approach (1) and (2), in order that the image quality and the gloss which were excellent in the film photo average may obtain, as for the 75-degree glossiness (JIS-Z - 8741) of the record table whole surface, it is desirable that it is 30% or more, and it is still more desirable that it is 50% or more.

[0040]

[Example] Although the following example explains this invention concretely, of course, the range of this invention is not limited by these. Moreover, especially the "section" in an example, and "%", unless it refuses, the "mass section" of solid content and "mass %" except water are shown.

[0041] The following ingredient was used in the following example and the example of a

comparison.

((A) Coating liquid) After carrying out grinding distribution of the synthetic amorphous silica (Japanese silica industrial company make, trademark:Nipsil HD-2) with a mean particle diameter of 3 micrometers by sand glider, grinding distribution was further carried out with the pressure type homogenizer (SMT company make, a trademark: extra—high voltage type homogenizer GM-1), and the mean particle diameter of a primary particle prepared 5% silica dispersion liquid A containing 15nm and the silica particle whose mean particle diameter of an aggregated particle is 100nm. The poly dimethyl diaryl ammoniumchloride (product [ made from SENKA ] trademark: uni-sense CP- 103) 15 section was added as a cationic compound in this silica dispersion-liquid A100 section, and it was made to thicken and condense. Grinding distribution actuation was repeated and the silica sol AK was prepared 6% until the mean particle diameter of an aggregated particle was set to 150nm in this silica—cationic compound floc particle. In this silica sol AK100 section, the polyvinyl alcohol (whenever [ Kuraray Co., Ltd. make, trademark—VA-135H, polymerization—degree:3500, and saponification ]: 99% or more) 24 section was mixed 5%, and coating liquid A was prepared in it.

[0042] ((B) Coating liquid) Like dispersion liquid A, actuation of grinding distribution was repeated and 10% silica dispersion liquid B whose mean particle diameter of an aggregated particle is 800nm were prepared. The polyvinyl alcohol (whenever [ Kuraray Co., Ltd. make, trademark-VA-135H, polymerization-degree:3500, and saponification ]: 99% or more) 40 section was mixed 5% in this silica dispersion-liquid B100 section, and coating liquid B was prepared.

[0043] [Coating liquid C] Coating liquid C as well as the coating liquid A for ink absorbing layers was adjusted. However, the polyvinyl alcohol (whenever [ Kuraray Co., Ltd. make, trademark-VA-117, degree-of-polymerization:1700, and saponification ]: 99% or more) 24 section was used 5% 5% instead of the polyvinyl alcohol (whenever [ Kuraray Co., Ltd. make, trademark-VA-135H, degree-of-polymerization:3500, and saponification ]: 99% or more) 24 section.

[0044] [Coating liquid D] The poly dimethyl diaryl ammoniumchloride (product [ made from SENKA ] trademark: uni-sense CP- 103) 15 section was added as a cationic compound in said silica dispersion-liquid A100 section, and it was made to thicken and condense. Actuation of grinding distribution was repeated until the mean particle diameter of an aggregated particle was set to 700nm in this silica-cationic compound floc particle, and the silica sol AK was prepared 6%. The polyvinyl alcohol (whenever [ Kuraray Co., Ltd. make, trademark-VA-135H, polymerization-degree:3500, and saponification ]: 99% or more) 24 section was mixed 5% in this silica sol AK100 section, and coating liquid D was prepared. In addition, in each above-mentioned grinding distributed processing, the diameter of a silica primary particle is before and after processing, and it was changeless.

[0045] The needle-leaved tree bleached kraft pulp (NBKP) which carried out beating until [production of base material] standard freeness (JIS P-8121) was set to 250ml, and the broad-leaved tree bleached kraft pulp (LBKP) which carried out beating until standard freeness was set to 280ml were mixed at a rate of a mass ratio 2:8, and the pulp slurry of 0.5% of concentration was prepared. 0.1% of anion-ized polyacrylamide resin and 0.7% of polyamide polyamine epichlorohydrin resins are added 2.0% of cation-ized starch, and alkyl ketene dimer 0.4% on the basis of pulp bone-dry mass, and it fully stirred and was made to distribute in this pulp slurry. The long network machine was presented with the pulp slurry of the above-mentioned presentation, paper making was carried out, and the stencil paper of 3 was manufactured [ the obtained wet paper web ] for a dryer, size press, and a machine calender through, the basis weight of 180g/m2, and the consistency of 1.0g/cm. Carboxyl denaturation polyvinyl alcohol and a sodium chloride are mixed with the mass ratio of 2:1, this is added to water, the heating dissolution is carried out, it prepares to 5% of concentration, and the size press liquid used for the above-mentioned size press process is this to both sides of paper A total of 25 ml/m2 It applied by coverage and the stencil paper for base materials was obtained.

[0046] After performing corona discharge treatment to both sides of said stencil paper for base materials, with a Banbury mixer, carry out mixed distribution and it is prepared to them. And the amount of coating is the polyolefin resin constituent which has the following presentation on the felt side face of stencil paper 25g/m2 It is made to become. Moreover, the amount of coating is

the same polyolefin resin constituent as the above on the wire side face of stencil paper 20g/m2 So that it may become the cooling roll which carries out a spreading laminating using the melting extruder (melting temperature of 320 degrees C) which has T mold die, and has a mirror plane for the above-mentioned layer on a felt side face — moreover, the resin layer on a wire side face was drawn on the cooling roll of a split face, and cooling solidification was carried out. Surface smoothness (Oken type, J.TAPPI No.5) is 6000 seconds, and opacity (JIS P-8138) was acquired for 93% of base material.

The long-chain mold low-density-polyethylene resin (consistency 0.926g/cm3 and melt index 20g / 10 minutes) 35 section, (Polyolefin resin constituent for base materials) The low-density-polyethylene resin (consistency 0.919g/cm3 and melt index 2g / 10 minutes) 50 section, The anatase mold titanium-dioxide (Ishihara Sangyo [ Kaisha, Ltd. ] make trademark: A-220) 15 section, The zinc stearate 0.1 section, the anti-oxidant (Ciba-Geigy make,

trademark:Irganox1010) 0.03 section, the ultramarine blue (shrine make trademark: the first formation blue-shade ultramarine blue No. 2000) 0.09 sections, the fluorescent brightener (Ciba-Geigy make, trademark:UVITEXOB) 0.3 section.

[0047] On the front face of the example 1 aforementioned base material, solid content coverage is said coating liquid B at MEIYABA 30 g/m2 It applied so that it might become, and it dried, and the inside ink absorbing layer was formed. It is a boric acid content solution (concentration: 1.5%) on this inside ink absorbing layer 5 g/m2 It applies by coverage, it sets in the condition that it does not dry, and solid content coverage is said coating liquid A at MEIYABA on it 5 g/m2 The ink jet record sheet which applied so that it might become, dried with hot air drying equipment (temperature: 100 degrees C, wind-speed:8m/second), and formed the outside ink absorbing layer was obtained.

[0048] On the front face of the PET film (trademark [ the Toray Industries, Inc. make and ]:lumiler T, thickness: 75 micrometers) used as an example 2 shaping side, the amount of solid content coating is said coating liquid A at MEIYABA 5 g/m2 It applied so that it might become, and it dried, and the outside ink absorbing layer was formed. It is a boric acid content solution (1.5% of concentration) on this outside ink absorbing layer 3 g/m2 It applies by coverage. On this solution layer, solid content coverage is said coating liquid B at MEIYABA 30 g/m2 It applies so that it may become. On this humid inside ink absorbing layer, commercial stencil paper (the Oji Paper Co., Ltd. make, a trademark:O.K. coat, and basis—weight 127.9 g/m2) was dried with lamination and hot air drying equipment (temperature: 100 degrees C, wind—speed:8m/second), the PET film was exfoliated after an appropriate time, and the ink jet record sheet was obtained.

[0049] The ink jet record sheet was obtained like example 3 example 1. However, coating liquid C was used instead of coating liquid A.

[0050] The ink jet record sheet was obtained like example 4 example 1. However, coating liquid D was used instead of coating liquid A.

[0051] The ink jet record sheet was obtained like example of comparison 1 example 1. However, water was used instead of the boric acid content solution (1.5% of concentration).

[0052] The ink jet record sheet was obtained like example of comparison 2 example 2. However, water was used instead of the boric acid content solution (1.5% of concentration).

[0053] The ink jet record sheet was obtained like example of comparison 3 example 1. However, the way sand content solution (1.5% of concentration) was used instead of the boric acid content solution (1.5% of concentration).

[0054] Measurement evaluation of the visual appearance, the glossiness, and printing concentration of seven sorts of ink jet record sheets obtained in examples 1-4 and the examples 1-3 of a comparison was carried out by the following approach. The result is shown in Table 1. The visual appearance of a [visual appearance] ink jet acceptance layer was evaluated in accordance with the following criteria. O What reached and was displayed as \*\* is level which is satisfactory practically.

O : although there is no crack in a spreading side and a fitness \*\*:spreading side has a crack, the level x:spreading side which is satisfactory practically has many cracks, and it is level [0055] with practically difficult use. According to [glossiness] JIS-P8142, 75-degree glossiness of the blank

paper section was measured.

The ink jet printer (the Epson make, trademark-M-800C) was used for the [printing concentration] sample offering ink jet record sheet, the mark counterpart was used for Kurobe solid, the Macbeth reflection density meter (made in Macbeth, RD-914) was used for the depth of shade, and it measured. The figure shown in front Naka is the average of 5 times measurement.

[0056] The xenon weather meter (the Suga Test Instruments Co., Ltd. make, 63 degrees C, 90%) was used for it, light was irradiated for 48 hours, and the ink jet printer (the Epson make, trademark-M-800C) estimated the result as follows to it, after \*\*\*\*(ing) a portrait image (highly minute color digital standard image data, N1, Japanese Standards Association) to a [light-fast] sample offering ink jet record sheet.

O: fading is good few.

x: Fading progresses and they are those with a problem.

To the [ink absorptivity] sample offering ink jet record sheet, the ink jet printer (the Epson make, trademark-M-800C) estimated the absorption situation of a mark counterpart and ink for the image (highly minute color digital standard image data, N5, Japanese Standards Association) of a bicycle as follows.

O: there is no blot and the line has clarified.

x: There is a blot and the line is crushed.

# [0057]

# [Table 1]

İ	目視外観	光沢値	印字濃度	耐光性	インク
					吸収性
実施例1	0	50	2. 27	0	0
実施例2	0	6 1	2. 35	0	0
実施例3	Δ	46	2. 27	0	0
実施例4	Δ	4 5	2. 22	0	0
比較例 1	×	25	2. 21	×	×
比較例2	×	29	2. 24	×	×
比較例3	×	29	2. 21	×	×

### [0058]

[Effect of the Invention] The manufacture approach of the ink jet record sheet of this invention can form an ink absorbing layer with sufficient spreading nature, the ink absorptivity and lightfastness are good and, moreover, defects, such as a crack, can manufacture efficiently few glossy high ink jet record sheets.

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### **DESCRIPTION OF DRAWINGS**

[Brief Description of the Drawings]

[Drawing 1] The cross-section explanatory view showing the laminated structure of the ink jet record sheet obtained by this invention approach (1) and (2).

[Drawing 2] The explanatory view showing the process of this invention approach (2).

[Description of Notations]

- 1 -- Base material
- 2 -- Inside ink absorbing layer
- 3 -- Outside ink absorbing layer
- 4 Imprint base material
- 5 Boric acid content solution spreading layer
- 6 -- Ink jet record sheet

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# **DRAWINGS**

